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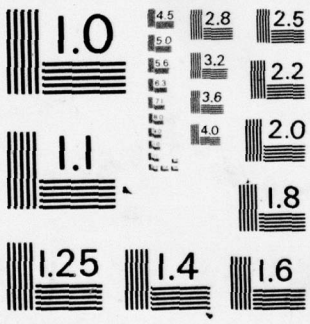

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HOT CORROSION OF HIGH TEMPERATURE ALLOYS.

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20th August,1976.

Final Scientific Report : 15 May 1972-14 May 1975.

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Hot corrosion is a form of accelerated oxidation of alloys which can occur in combustion gases in the presence of impurities. The characteristics of the reaction are defined by describing practical examples, and then the results of a variety of laboratory experiments are considered in relation to the practical process. The temperature dependence and kinetics of the corrosion are briefly presented, and the effect of alloying elements is discussed; high chromium contents are required for good corrosion resistance,

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but there is no general agreement on the effect of other alloy elements. A number of mechanisms for hot corrosion are described and discussed in relation to the practical results.

A list of publications resulting from the work partially supported by this Grant is attached.

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HOT CORROSION OF HIGH TEMPERATURE ALLOYS

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1. Introduction

This contract has been used to supplement work in progress in the Department on the general topic of hot corrosion in nickel and cobalt-base superalloys under conditions relevant to the gas turbine. In particular, it has been possible to consider the mechanisms of hot corrosion and to draw together principles established in different research programs funded from other sources. The Second Interim Scientific Report, for example, examined the hot corrosion of Ni-Cr-Al-Mo alloys using the technique of presulphidation followed by oxidation, and other papers discussed the role of sulphur in hot corrosion. A number of papers have made reference to the support of the U.S. Air Force, and are listed in the next section.

For the Final Report, the opportunity has been taken to review the general field of hot corrosion, and this review forms the main body of the report.

2. Published Papers Acknowledging Partial Support

(i) "Hot Corrosion of Nickel-Base Alloys Containing Al and Mo", J.Stringer, M.E.El-Dahshan and D.P.Whittle, Werkstoffe u-Korrosion, 25, (1974) 910-916.

(ii) "Hot Corrosion of Cobalt-Base Alloys", J.Stringer, Ceramika 21 (1974) 237-245).

(iii) "The Role of Sulphur in Hot Corrosion", J.Stringer and M.E.El-Dahshan, Proc. 1974 Conf. on Gas Turbine Materials in the Marine Environment (J.W.Fairbanks and I.Macklin,eds.) Metals and Ceramics Information Center Report MCIC-75-27, pp. 161-182.

(iv) "The Hot Corrosion of Nickel-Base Superalloys : The Effect of Molten Salt Chemistry", J.Stringer and D.P.Whittle in "Metal-Slag-Gas Reactions and Processes" (Z.A.Foroulis and W.W.Smeltzer, eds.), Electrochemical Society, Princeton (1975) 665-677.

(v) "Hot Corrosion of High Temperature Alloys", J.Stringer. To be published in the proceedings of The Electrochemical Society Symposium on Properties of High Temperature Alloys, Las Vegas, Oct. 1976.

(vi) "Hot Corrosion in Gas Turbines" J. Stringer. To be published in Annual Reviews of Materials Science.

HOT CORROSION OF HIGH TEMPERATURE ALLOYS

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Abstract

Hot corrosion is a form of accelerated oxidation of alloys which can occur in combustion gases in the presence of impurities. The characteristics of the reaction are defined by describing practical examples, and then the results of a variety of laboratory experiments are considered in relation to the practical process. The temperature dependence and kinetics of the corrosion are briefly presented, and the effect of alloying elements is discussed; high chromium contents are required for good corrosion resistance, but there is no general agreement on the effect of other alloy elements. A number of mechanisms for hot corrosion are described and discussed in relation to the practical results.

1.1. Introduction

Hot corrosion is a form of accelerated oxidation which affects alloys exposed to high-temperature combustion gases containing small amounts of certain impurities. This definition could, of course, cover a large number of processes having quite different character, and in order to interpret the phenomenon it is necessary to define the nature of the attack much more precisely. This is of particular importance in relation to the design of laboratory experiments, and the interpretation of their results.

The term was coined to describe the corrosion of a number of components in service; and these share certain common features, both in the morphology of the corrosion and in the nature of the environment. It is logical therefore to define hot corrosion in relation to similar criteria; and to this end some examples of hot corrosion will be

briefly examined.

1.2. Some Examples of Hot Corrosion in Practice.

The earliest example was the accelerated wastage of stainless steel superheater supports in a marine boiler (1). The cause of this was traced to sea water contamination of the fuel, and the corroded components were covered with a white deposit which proved to be sodium sulphate. In the 1950's several examples of accelerated corrosion in gas turbines were reported: Archdale (2) refers to tests run on a Proteus engine with Nimonic 90 blades and vanes in 1955 using fuel containing 0.57 - 0.76% S. Salt was injected into the air intake at 1.07 ppm, and the test ran for 225h: it proved to be necessary to increase the turbine inlet temperature to maintain the specified power and this turned out to be due to the deposition of a layer essentially of anhydrous sodium sulphate on the stator blades. The deposit contained approximately 5% each of magnesium and calcium sulphates, and some carbonaceous matter; but no chloride was detected. Several authors (3) reported corrosion of 713C blades and vanes from aircraft engines used for coastal missions in South East Asia, and from marine engines: severe attack was observed after operating times as short as 250h. Corrosion of this alloy was also observed in industrial engines, for example in an engine burning natural gas with very low sulphur located on the Canadian prairie: the turbine inlet temperature was 788°C. (4) Erdös (5) shows an example of severe corrosion in a 713C vane from an engine burning natural gas with 2-4% H_2S with Ca and Na impurities in the intake air after 1 year at turbine inlet temperatures in the range 700 - 750°C. Wall and Michael (4) also report corrosion in a turbine burning natural gas in Japan: the alloy appears to have been Udimet 700, and the turbine inlet temperature was only 732°C; but the gas contained 10-13% H_2S and the engine was located near the sea coast.

Conde (6) reports failures of Nimonic 90 first stage nozzles in Allen 500 kW turbines at a maximum temperature of 735°C attributable to ingestion of considerable amounts of sea water; similar severe attack of the alloy was encountered in a marine Proteus engine in a Brave Borderer patrol boat.

Several cases of hot corrosion attack, then called "black plague" were encountered on Nimonic 100 first stage blades from Bristol-Siddeley Olympus engines (3) : a report by Smith et al (7) appears to be the first, dated 1957; the attack was observed after 401h running, and the blade temperature would have been approximately 870°C. Several cases of corrosion of Nimonic 105 blades in marine and industrial engines are reported in the literature (3). Rolls-Royce (8) observed severe corrosion of Nimonic 105 blades in a Spey engine on a test bed after 622h of a planned 1000h simulated Trident flight:

the structure of the alloy showed that the metal temperature had not been significantly above 950°C. In this case, the source of the sulphur was believed to be chemical fertilizer used by farmers in fields adjacent to the test establishment. Page and Taylor (9) report cases of hot corrosion of Nimonic 115 in an industrial Avon engine after 1900 running hours with a maximum operating temperature of 900°C with high levels of salt in the fuel.

Udimet 500 is generally very resistant, but Quigg and Schirmer (10) show a corroded first stage blade from an engine which had completed 1800h in domestic air-line service since overhall. Hussey et al (11) describe experiences with two Westinghouse W171 gas turbines installed at the Miraflora station of the Panama Canal Company, overhauled and put in service in 1965 burning a fuel containing less than 10 ppm Na, less than 4 ppm V, less than 10 ppm Ca and less than 1.8% S. Although some corrosion was expected, even at the reduced turbine inlet temperature of 746°C, the corrosion after 6375h operation was extensive. The first stage vanes in both engines were Udimet 700, and showed extensive damage. After treating the fuel so that the vanadium averaged 2.5 ppm and the sodium 0.5 ppm, there was only minor corrosion after 5000h.

Bergman et al (12) notes that in similar aircraft engines Udimet 700 has served most reliably, whereas 713C has been subjected to severe hot corrosion. However, Donachie et al (13) show a first stage Udimet 700 from a marine engine after 1100h showing severe hot corrosion, but again they remark that in aircraft engines operated where sporadic salt ingestion occurs, slight distress due to hot corrosion of 713C has occurred while Udimet 700 operated under the same conditions has been free from hot corrosion attack.

Waspalloy is another alloy regarded as highly resistant, but Hamilton et al (14) remark that they have seen isolated cases of hot-corrosion of Waspalloy after long time service at temperatures which should have been below 730°C; the same was true of Inco 901, A286 and 16-25-6 alloys. Møller (15) has shown an example of very severe corrosion of Nimonic 80A after 27000h service at 700-730° in a turbine burning blast furnace gas.

This summary of in-service corrosion is not intended to be exhaustive, although in fact the literature is not very extensive: companies manufacturing gas turbines are not generally very eager to provide extensive information on hot corrosion failures in their engines. In the case of the more recent engines, the situation is further complicated by the fact that few alloys are used in uncoated condition, and this is particularly true of the less-resistant alloys.

1.2. Morphology of Hot Corrosion.

Figure 1(a) shows the concave surface of a Nimonic 100 first-stage turbine blade from an Olympus engine after 401h running at approximately 870°C. Figure 1(b) shows a section of a similar blade, and Figure 1(c) shows the corrosion product at higher magnification. There is an outer oxide layer, rather porous; an intermediate layer of mixed oxide and metal, and finally an inner layer consisting of fine lighter-grey particles in a metal matrix. This innermost layer is shown in more detail in Figure 1(d). All these figures are taken from Smith et al (7). The outer oxide layer is essentially NiO, with some $NiCr_2O_4$ spinel. The intermediate layer is essentially Ni-rich fragments in a Cr_2O_3 matrix although again there is some spinel. The light grey particles are chromium-rich sulphides, and the metal in the inner layer is depleted in chromium. Very similar pictures of the corrosion of 713C blades operated in the Pacific for 600h are shown by Schirmer and Quigg (16).

The extent of the internal sulphide layer can vary considerably from being virtually absent, through a thin band of fine discrete sulphide particles through to very heavy interconnected sulphide networks. Figure 2 shows a particularly severe case of internal sulphidation of a Nimonic 105 blade, originally pack aluminised, after operation in a marine Proteus turbine for only 600 hours (6).

A number of investigators at Rolls-Royce pointed out that the same alloy in the same engine will exhibit a fairly general attack in marine applications, whereas in industrial applications there is localised corrosion, with "wart-like growth" in an otherwise un-corroded surface (see for example Page and Taylor (9)). Roberts (17) referred to the former as "sulphur-assisted oxidation" and remarked that in this case the sulphides appeared to be chromium-rich; whereas the "crater-flux" attack on industrial turbines appeared to require the formation of the molten $Ni-Ni_3S_2$ eutectic.

The matter of the composition of the sulphides has been the cause of some controversy. Analyses of the sulphides in corroded blades removed from service show them to be nearly always chromium-rich: more than one sulphide may be present at the same time in complex alloys. Hancock (18) pointed out that in severely corroded specimens (such as that shown in Figure 2) the sulphides had a morphology which he termed "liquid-like"; and suggested that the sulphides might have beem the liquid Ni_3S_2-Ni at temperature, and had reacted with the chromium in the alloy on cooling; some laboratory experiments suggested that this might be possible. Actually, the blades in an aircraft engine will cool very rapidly when the flame is turned off, since the compressor continues to spin blowing cold air through the turbine. Furthermore, the morphology of the sulphides formed when the liquid nickel sulphide is really present looks quite different: this interesting hypothesis has now been abandoned. Nevertheless, in a small number of cases

significant amounts of nickel sulphides have been observed in severely corroded blades; and McKee et al (19) have suggested that a thin layer of nickel sulphide is usually present between the chromium-rich sulphide and the chromium oxide.

1.3. Kinetics of Hot Corrosion

Naturally, there is very little information on the detailed kinetics of hot corrosion from examination of in-service failures. However, there is some indication of the existence of an incubation period, i.e. an initial period during which there is no accelerated oxidation: the attack is then initiated and propagates relatively rapidly. Belcher et al (20) appear to have been among the first to remark on the existence of an incubation period for blades in gas turbines, noting that no case of hot corrosion of Nimonic 100 had been reported unless they had been operated for at least 100 hours at 900°C. Others have reported cases where blades had been found to be free of corrosion during a routine inspection after (for example) 2000 hours, but failed because of hot corrosion after a further few hundred hours. This does not in itself prove the existence of an inherent incubation period, because it might be related to some unspecified change in operating procedure, or some large influx of impurities. Nevertheless, the balance of the evidence appears to favour the concept of an incubation period for hot corrosion.

1.4. Temperature Dependence of Hot Corrosion

Again, the evidence from practice is not very clear and sometimes contradictory. In the case of the broad-front attack characteristic of aviation or marine engines, the region of severe attack on the blade seems to coincide with the high-temperature region. On some blades, however, the maximum attack is not at the point at which the metal temperature would have been highest, but a little away from this, so two notches develop on the leading edge on either side of the mid-chord position. This implies a temperature at which the attack is a maximum. However, the "wart-like growth" corrosion of industrial turbine blades appears to follow no such simple pattern (9): sometimes the area of heaviest corrosion is the blade shroud, where the temperature would be expected to be relatively low (less than 700°C for a maximum blade temperature of 940°C (21). There is a general belief that below 750°C there is little chance of attack although there are some cases of corrosion at lower temperatures than this; attack seems to diminish above 900°C, and be virtually absent above 950°C, although few engines run with metal temperatures higher than this anyway. There is an accelerated oxidation which may take place at high temperatures, but it appears to be different from hot corrosion, and sulphur does not appear to play a part .

1.5. Nature of the Corrosive Deposit

Hot corrosion is associated with the formation of a corrosive deposit on the hot component. It is widely believed that the deposit must be molten for corrosion to occur, but this has not been definitely established: one or two authors have reported hot corrosion attack under solid deposits in laboratory tests. It is perhaps necessary to subdivide the hot corrosion process a little further, since the term is used to describe accelerated attack under two types of deposit: vanadium rich, and sodium sulphate rich. However, in most gas turbine practice the latter form of attack is more common, and vanadium probably acts principally to modify the sodium sulphate. This point will be examined later.

It has already been reported in section 1.1. that in early cases of severe hot corrosion substantial amounts of sodium sulphate were present. Tschinkel (22) has reported the composition of the deposits on turbine airfoils from air lines after 1000 to 5000 hours operation: the compositions varied widely, but the deposit was essentially a mixture of calcium, sodium and magnesium sulphates: usually the calcium was in a slight excess, and the amount of magnesium was relatively small. Sometimes a little silicon was present. The amount of the deposit could be as much as 8 mg/cm^2, there being considerably more on the vanes than on the blades. Hussey et al (11) identified a number of constituents in the deposit on the U500 blade after one year's operation using treated fuel (see section 1.1) including oxides, sulphates and vanadates of nickel and cobalt, hematite, and $Na_2Mg(SO_4)_2 \cdot 4H_2O$, which they comment is the hydrated product of a 50 : 50 mixture of sodium and magnesium sulphates solidified from the melt. The melting point of the mixture is 621°C, compared to 884°C for anhydrous sodium sulphate. The authors believe this to be an important corrosive constituent of the deposit, and several Westinghouse laboratory tests have used it as the corrodent. In contrast, $CaSO_4$, has little effect on the melting point of sodium sulphate.

The results of Archdale (2) have already been mentioned: an important point is that in that case some carbonaceous matter was detected in the deposit. Bessen and Fryxell (23) have commented that carbon is deposited on blades in practice, and can markedly enhance corrosion.

Sodium chloride is seldom detected in the deposit, although recent papers have reported small amounts present in deposits formed in marine applications.

1.6. Source of the Corrosive Deposit

It appears likely that the important constituent of the corrosive

deposit is sodium sulphate, with its properties perhaps modified by other constituents. The source of the sodium may be either the fuel or the intake air. Sodium in the fuel can be present either as an oil-soluble compound or, more commonly, as a result of sea-water contamination; sodium in the air is normally present as an aerosol of sea-salt. Sometimes sodium salts can be present in the air above deserts containing salt deposits. In sea water the majority of the sodium is present as sodium chloride, but approximately 11% is present as sodium sulphate.

Sulphur is present in the fuel: aviation kerosenes typically may contain 0.40 weight % sulphur (JP-5), although the average is nearer 0.10 wt.%; industrial turbines may burn light oils with similar sulphur contents, heavy distillates which may contain up to 2 wt.% sulphur or more (ASTM 3-GT), crude or residual oils which can be much higher. Industrial gas turbines may also burn gas: natural gas can vary from having almost no sulphur (present as H_2S) to quite sour gases containing several per cent H_2S. Sulphur can on occasion be introduced in the intake air: the ingestion of sulphur-containing fertilizers by test-bed engines has been referred to above, and aircraft flying near an active volcano in Iceland suffered severe hot corrosion attributed to the ingestion of sulphur-containing gases.

On thermodynamic grounds, sodium chloride is unstable in the presence of quite small concentrations of sulphur in an oxidising environment. DeCrescente and Bornstein (24) showed that the reaction

$$2NaCl + SO_3 + \tfrac{1}{2} O_2 = Na_2SO_4 + Cl_2$$

should go virtually completely to the right: more detailed calculations have been done by Tschinkel (22) amongst others for 5 ppm NaCl in the intake air, 0.5 wt.% sulphur in the fuel, showing that the concentration of NaCl is negligible below 1000°C with less than 2% of the sodium present as the chloride. At 1200°C up to 20% of the sodium will be present as chloride, 60% as NaOH and the remainder as the sulphate. However, there is considerable doubt of the applicablility of these equilibrium calculations since the residence time is very short: between entering the flame and passing the first stage blades represents about 5 ms, and the secondary air is present for an even shorter time. Hanby and Beer (25) have shown that the gas phase sulphation of NaCl is quite slow: very little sulphation takes place for the first 8 ms, and this does not depend on the salt concentration or the sulphur content of the fuel, and only slightly on the temperature.

The same authors have also demonstrated that the rate of evaporation of seal-salt aerosol particles is not particularly rapid, and thus the sodium chloride may not be present in the vapour phase. The sea -salt in the air is removed to some extent by the compressor: Besson and Fryxell (23) remarked that considerable quantities of salt

are condensed out in the compressor, and that it is not known whether the compressor deposits reach a steady state thickness or not; these deposits contain NaCl, but it is not reported whether they contain Na_2SO_4.

DeCrescente and Bornstein (24) suggested that sodium sulphate condensed on the cooler vanes and blades from the relatively hot gas: in this case, it should be possible to define a dew-point for a given salt concentration in the intake air and a given pressure in the turbine above which no condensation of salt should take place. Their calculations showed that for a pressure of 20 atm., an NaCl concentration of 1 ppm in the intake air, and assuming complete sulphation, the dew point was about 850°C; for 0.1 ppm NaCl it was about 780°C. However, several cases of condensation and corrosion in operating engines were observed where the salt concentrations were significantly below this. Morgan et al (26) found, in a Proteus engine at NGTE using a Nimonic 90 nozzle segment as a corrosion monitor, that with 0.05 ppm NaCl with turbine inlet temperatures in the range 660-780°C the alloy was corroded after about 1000 hours; with 0.005 ppm NaCl there was no corrosion after 1400 hours.

Besson and Fryxell (23) redetermined the vapour pressure of Na_2SO_4, and found that the values used by DeCrescente and Bornstein for their calculations were too high: Figure 3 shows dew points calculated using their vapour pressure data for two pressures and for complete sulphation of the NaCl and zero sulphation (i.e., all the Na_2SO_4 was that already present in the original sea salt). These results are much closer to engine experience, but it must be remembered that the salt concentration in the gas entering the combustion chamber may not be simply related to that entering the engine, and that much of it may not evaporate into the gas phase anyway. Besson and Fryxell also point out that if the engine is power cycled, salt may deposit at the lower temperatures and produce corrosion at the higher temperatures.

An alternative method of deposition is for the aerosol particles to deposit directly on the blades. This possibility has beem examined by Moore and Crane (27) who consider a number of different mechanisms, and calculate the doposition rate for NaCl particles. This may be particularly important if the salt collected in the compressor periodically breaks off (for example on start-up) and relatively large salt particles pass through the engine.

In summary, therefore, salt concentrations of over 0.01 ppm in the intake air may give trouble, but the exact mode of salt deposition on the metal surface is not well-understood. Little sodium chloride is present in the deposit, but the reasons for this are not clear: it cannot be deduced that chloride plays no part in the corrosion process.

Nothing has been said of vanadium, because gas turbines are not run with large vanadium concentrations in the fuel; the vanadium thus

serves mainly to modify the salt chemistry in ways which will be dealt with later.

1.7. Use of Fuel Additives.

The idea of using fuel additives to reduce the corrosion is about as old as the realisation of the cause of the attack. Traditionally, vanadium attack has been minimised by the use of an additive such as magnesium oxide, which reacts with the vanadium to form a high melting point magnesium vanadate which does not stick to the blade surfaces. Young and Hershey presented a thermochemical study of additives as early as 1957 (28) aimed at increasing the melting point of sodium sulphate. More recently, the idea of additives capable of forming stable compounds with sodium has been explored, and additives based on oil-soluble chromium compounds have been tested, with the aim of forming the stable sodium chromate. There have been claims that additives of this type have been very successful in restricting hot corrosion in marine environments, but few data have yet been published.

1.8. Effect of Alloy Composition

It is very difficult to draw many conclusions concerning the effect of alloy composition from the practical experience since it is unusual for different alloys to be used in the same type of engine in similar applications, and even then circumstances may differ. Nevertheless, one can make some general evaluations:

- B1900, IN 100, and Nimonic 100 are very poor in hot corrosion; probably in increasing order of resistance; and really cannot be considered for use without coating even in mildly corrosive situations.
  713C is poor, but many engines have run for many hundreds of hours with uncoated 713C hardware in circumstances which might be mildly corrosive.
  Udimet 700 will corrode, but in similar applications is better than 713C.
  Nimonic 105 has suffered hot corrosion on a number of occasions in marine and industrial turbines: it would seem to be comparable to Udimet 700.
  Nimonic 90 has exhibited severe corrosion in particularly aggressive circumstances.
  Udimet 500 is generally very resistant, but some cases of hot corrosion have been reported.
  Waspalloy, Hastelloy X and perhaps Nimonic 80A appear to be very resistant, although in each case some examples of hot corrosion have been reported.

Examination of the Table of composition of the alloys (Table 1) shows that this approximate order of merit correlates quite well with the chromium content of the alloys; and it is a general view that a minimum of 15% chromium is required for hot corrosion resistance. No other conclusions can be drawn from this list. In recent years several new alloys have been developed with the specific intention of securing good hot corrosion resistance with high strength levels, examples being IN738, Mar-M 432 and Udimet 710: all of these contain 15.5% chromium or more.

There is a view that cobalt-base superalloys are superior to nickel-base, although they have lower strength, particularly at intermediate temperatures. When engines are converted from aircraft use to industrial or marine applications, it is common to replace the relatively lowly stressed nozzle guide vanes with a cobalt-base alloy such as X-40 or Mar-M 509. However, these alloys have significantly higher chromium contents, and it is not possible to conclude from the in-service experience whether the cobalt matrix in itself confers any superior corrosion resistance.

2. Hot Corrosion Tests.

The first section has described the characteristics of the practical failure described as hot corrosion. Tests may have two quite distinct functions:

(1) To select alloys which will exhibit superior hot corrosion resistance in practice, or to assist in the design of superior alloys.

(2) To investigate the mechanism of hot corrosion.

For the first function it is not absolutely necessary that the corrosion produced in the test should resemble that in the practical situation. It is only necessary to demonstrate that there is a clear correlation between the results of the test and the behaviour of alloys in practice: thus, if a test can rank the eleven alloys described at the end of section 1.8 in the order shown, it is reasonable to suppose that another alloy which gives good results in the test will also behave well in the engine.

However, the chances of success are clearly much better if the test does produce a corrosion morphology as much like that encountered in hot corrosion failures as possible; and most engine builders feel in addition that the test environment should bear as close a resemblance as possible to that encountered in the engine. A turbine simulator which can approximate to the gas composition, pressure, velocity, and temperature of the real engine, using blade-like specimens stacked in an array resembling a wheel, cooled where appropriate, and perhaps

subjected to stress patterns similar to those experienced in practice, is very expensive. Furthermore, it is expensive to run: and it is apparent from what has gone before that if it were to simulate the real situation, alloys may not corrode for 1000 hours or so, yet still be unsatisfactory. In practice, the more expensive the simulator, the shorter runs can be carried out, and in order to get observable corrosion in the available time the conditions have to be made untypically severe. It is arguable that this destroys the validity of the simulation.

The majority view is that the effect of high pressure is only to modify the deposition conditions, and that consequently tests may be run at atmospheric pressure with only a modest increase in the salt concentration. Gas velocity must also have an effect on salt deposition, but it is usual for rigs to run at velocities rather lower than those in the engine. Although in some cases airfoil shaped specimens are used, in the majority of cases it is felt that the corrosion can be better characterised with cylindrical pin specimens. Accordingly, there are many atmospheric pressure "burner rig" test assemblies in use. Many of these use a combustion chamber from a small gas turbine, supplying air from compressors and burning fuel in the usual way. Salt may be added to the fuel, or the air, or sprayed into the hot combustion gases. These hot gases may then be ducted down a channel, or may issue freely from the nozzle of the combustion chamber; they then pass over an array of rod samples. In the majority of cases the rods are in a carousel mount, which is rotated in the gas stream. Since thermal cycling is thought to be important, there is often a capability of withdrawing the specimen assembly from the hot gas jet to allow it to cool, then replacing it.

A still simpler rig is that based on the General Electric small burner rig. In the original form this burnt fuel in air, but with a much simpler combustion chamber than that used in the gas turbine: the hot gases passed down a duct to pass over a carousel of specimens heated in an auxiliary resistance furnace. In the later version, the specimens are discs with holes cut in them, arranged loosely on pin supports.

While early investigators used weight change measurements to characterize the corrosion - either weight gain, or the weight loss after descaling - it has been generally accepted that the important manifestations of hot corrosion, particularly during the early stages, take place beneath the metal surface. Most laboratories now use a metallographic estimation of damage, following a scheme originally proposed by General Electric (12), in which two quantities are reported: the surface loss, and the maximum penetration.

In early investigations, General Electric used a salt concentration of 200 ppm and test periods of the order of 50 hours; but later changed to a lower salt concentration (5 ppm) and longer times

(1000 hours) because these gave better correlation with practice in marine environments (12).

As a result of the accumulation of a great deal of experience with the small burner rig, General Electric believe that it correlates well with engine experience (29,30). Similar correlations have not so far been demonstrated for other tests, although obviously different engine manufacturers must have confidence in the methods they are using, presumably based on unpublished correlations with operating experience. However, it must be remembered that most manufacturers have experience with a fairly limited number of alloys in any given engine for any given mission; and this limits the validity of any correlations.

Those concerned with alloy development have used a simpler set of laboratory tests, aimed at giving comparative information on a wide range of alloys relatively quickly. The earliest of these was the half-immersion or crucible test, in which a suitable salt mixture was melted in a crucible, and a rod of the test alloy immersed up to its midpoint in the salt. The atmosphere above the salt was usually laboratory air. An early investigation using this method was that of Lewis and Smith (31), and indeed the technique was used by International Nickel until very recently. Another investigation using the crucible method was that of Graham et al (32), who used 99% Na_2SO_4, 1% NaCl salt mixtures in a 30 ml. silica crucible at test temperatures in the range 871-1093°C for times of 1, 2, 5 and 25 hours. They showed the correlation between their results and the Pratt and Whitney burner rig results, and at first sight the correlation curve looks quite good: but in fact this is because the correlation graph is based almost wholly on very poor alloys: the correlation for moderate alloys is not demonstrated, and their ranking table shows 713C to be worse than IN 100, which is to say the least unlikely. The conditions in the crucible test are quite unlike those in the real situation, and the form of attack is generally dissimilar: it can be justified therefore only on the basis of its correlation with practice. One view is that if an al alloy can stand up to the very severe environment of the crucible test, it can certainly stand up to the conditions in an engine; a further point is that it was used as the principal screening technique by International Nickel in the development of a successful group of alloys including IN 738. This is perhaps correct: but it may be that alloys quite acceptable in practice might have been eliminated by the test.

Recently, International Nickel have replaced the crucible test with the salt-shower test, in which a specimen is oxidised in a vertical furnace through which solid salt is showered continuously.

The remaining techniques are concerned with the study of the corrosion mechanism. It is not necessary for these techniques to rank alloys in the correct order, nor indeed to reproduce hot corrosion morphologies; provided the aspect of the reaction which is being studied is accurately modelled. The dange is that success in one limited aspect - for example, the morphology of the sulphide distribut-

ion - may be taken to justify accepting all other results of the test, even when it was not designed to model these aspects. The reverse danger is equally real.

A technique which has provided a great deal of information on some aspects of the reaction mechanism is the salt-coated test, in which a specimen is first coated with a suitable salt mixture, then oxidised in an appropriate gas stream. A modification of this is to replace the salt coating periodically. The technique is obviously ideally suited to thermogravimetric methods, so kinetic curves of corrosion can easily be obtained. The composition and thickness of the salt layer can be selected to model those found in practice, and if desired the gas composition can also be adjusted to model real combustion atmospheres.

The sulphidation parts of the process can be modelled to some extent by oxidising specimens in O_2 - SO_2 mixtures, or by presulphidizing specimens and oxidizing them. An important criterion here is probably the duplication of the sulphide morphology in hot corrosion, and perhaps also a duplication of the morphology of the development of the metal/oxide mixture layer.

A recent technique which has considerable potential both as a mechanistic research tool and a test technique, is the modified Dean rig (33). The rig uses a furnace having two zones whose temperatures can be controlled independently, and between which the temperature changes smoothly. In one zone the specimen is placed, and in the other a boat containing a suitable salt. An appropriate gas is passed over the salt boat, and salt is evaporated into it. The salt-laden gas then passes over the specimen: if the specimen is cooler, the salt will condense. Corrosion is usually evaluated metallographically, but recently a gravimetric Dean rig has been developed (34). It will become clear later that one model of hot corrosion is electrochemical, and a number of investigations have used fused salt electrolytic cells to study aspects of the electrode reactions. Shores (35) has developed an anodic polarization technique for the evaluation of alloys in reagent grade sodium sulphate at 906°C in air, using a three electrode cell. The results are correlated with the results of the small burner rig and show quite good correspondence over a reasonable range of alloys. However, while the small burner rig gives virtually the same corrosion resistance for Udimet 700 and 713C, the anodic polarization technique shows Udimet 700 appreciably worse than 713C: as shown in Section 1 this is the reverse of the practical situation. Nevertheless this is a very interesting development, in principle capable of screening materials quickly, and also capable of examining the effect of possible variations in salt chemistry.

The problem of assessing the reality of test procedures and the difficulty of calibrating tests against in practice behaviour is well-known, and the Hot Corrosion Task Force of the Gas Turbine Panel of ASTM organised a Round Robin test of six alloys (713C. IN 100. IN 738.

Mar-M 421, Udimet 500 and Udimet 700) during 1969 (36). Results from 15 participants were received, 13 using some form of burner rig. The majority of the tests were at 1650°F (900°C The correlation between the different investigations, shown in Table 2, do not seem bad at first sight, but there are several anomalies. There is little doubt that in practice U500 would have the best corrosion resistance; IN 738 and Mar-M 421 were designed with the criteria of having corrosion resistance equal to U500 but with superior strength, and perhaps IN 738 came closer to having the necessary corrosion resistance; as has been shown above U700 is rather better than 713C, and IN 100 is very significantly worse. Tests ranking U700 the best of the six alloys, for example or ranking IN 100 above 713C, should be regarded with some suspicion.

3. Results from Laboratory Tests

3.1. Kinetics of Hot Corrosion

Relatively few of the laboratory experiments have been greatly concerned with kinetics, most testing for a fixed period and then assessing the damage. Because of the non-protective nature of the corrosion it might be anticipated that the rate of attack would be constant (linear rate law), but Kaufman (37) determined the rate of attack of several nickel-base alloys in the GE burner rig for times up to 100 hours using 200 ppm salt, and found that the majority corroded according to an approximate parabolic rate law, only a couple of alloys showing a transition to a linear rate.

A number of investigations concerned with mechanistic studies have reported kinetics. Hardt et al (38) oxidised nickel in dry oxygen at 900°C with and without a coating of sodium sulphate for times of the order of 100 minutes. With the salt coating the initial rate of weight gain was extremely rapid, but slowed after 10 minutes or so: at the end of 40 minutes the rate was comparable to that of the uncoated specimens. If the sodium sulphate was removed from the specimen by washing, the rate immediately slowed to that of the uncoated alloy. Several authors have reported similar curves, but Johnson et al (39) have pointed out that pure cobalt behaves differently: at 900°C in oxygen at 1 atm. pressure cobalt with a coating of sodium sulphate oxidises rather more slowly than does pure cobalt, for times up to 80 hours (see also Hardt et al (38)). Goebel and Pettit (40) have reported a similar effect at 1000°C, but found that in some cases an accelerated attack could be induced at lower oxygen pressures.

However, Co-7.5 wt.% W alloys did show an accelerated oxidation when coated with sodium sulphate (39); Co-7.5 wt.% Ta did not. These and similar results will be discussed later.

Relatively few kinetic data have been produced from rig tests. Rolls-Royce (1971) Ltd have reported a number of corrosion rate curves from their burner rig (3). Nimonic 105 corrodes relatively slowly for

some hours at 870°C, 4 ppm salt; but after 80 hours or so the rate shows a significant increase. 713C behaves in a similar manner, although corroding much more quickly. The corrosion rate of 713C and Nimonic 115 are rather lower at 1050°C; Nimonic 105 corrodes a little quicker but there is little or no incubation period with the rate decreasing towards the end of the 120 hour test; at that time it is perhaps a little slower than at the lower temperature (see also Page and Taylor (9)).

3.2. Temperature Dependence of Hot Corrosion

Lewis and Smith (31) used a 1-hour crucible test to study the corrosion of a number of alloys in the temperature range 700-1000°C, determining the corrosion in terms of weight loss after descaling. The salt was a mixture of sodium sulphate and sodium chloride, and for some alloys with some salt mixtures, the corrosion showed a maximum as a function of temperature. Thus, Nimonic 80A in 25% NaCl salt mixtures showed a maximum attack at 900°C, decreasing very markedly up to 1000°C; Nimonic 105 showed a monotonic increase in corrosion with temperature.

Walters (41) used a burner rig with airfoil-shaped specimens, 120 hours at peak specimen metal temperatures of 871° and 955°C. The temperature profile was determined over the specimen for each of these peak temperatures, and the corrosion contours measured were then transformed to corrosion versus temperature contours. There was reasonable correspondence between the results for temperatures below 870°C for the two tests. Salt concentrations of 4 and 8 ppm were used. This test showed very clear upper and lower threshold temperatures: outside these bounds there was no corrosion. This agrees with the observations reported in Section 1.4. The threshold temperatures differed significantly for different alloys: for example, the threshold temperatures were 780° and 950°C in the case of B1900 for 8 ppm salt; 890°C and greater than 955°C in the case of Udimet 700. It would appear therefore that they do not correspond to the melting point of the salt and the dew point respectively, which would be the simplest explanation. The General Electric small burner rig results apparently show a similar temperature dependence (42): both upper and lower threshold temperatures shift to lower values as the salt concentration is decreased and the test time increased.

However, Ryan et al (43), using a rather different test, found a monotonic increase in corrosion over the temperature range 927 - 1093°C. Their test consisted of heating 16 specimens of the same shape as a T56 turbine blade in a furnace, the specimen assembly rotating at 1800 rpm. After 1.5 minutes heating, the specimens were lowered into a cooling chamber for 0.5 minutes, where they were sprayed with a sodium sulphate solution. The combustion gas in the furnace contained from 10% to less than 1% excess oxygen, depending

on the test temperature. A complete test was 500 cycles. Eight alloys were tested, but all showed the same general temperature dependence.

Page and Taylor (9) remark that 870°C seems to be close to the peak "sulphidation" temperature for most metals, but that Nimonic 105 has a peak temperature lower than this. However, graphs of temperature dependence of penetration are shown for the temperature range 870 - 1050°C, and these show a monotonic increase for X-40, little change for IN 738 and Nimonic 105, and marked minima at 950°C or so for IN 100, Udimet 700 and M432. This is because another high-temperature process becomes important at 1000°C or so.

3.3. Effect of Salt Composition

Many of the early investigators reported that molten sodium sulphate by itself was not very corrosive. Simons et al (44) reported that crucible tests using sodium sulphate were very irreproducible, and where corrosion was experienced they attributed it to the presence of carbon or the contamination of the specimen by handling. Sykes and Shirley (45) also found that pure sodium sulphate had little effect, but the addition of as little as 0.3% NaCl produced a rapid increase in scaling rate. Waddams et al (46) also found that mixtures of 99% Na_2SO_4-1% NaCl were much more corrosive than the pure sulphate; pure NaCl also produced heavy corrosion in their crucible experiments. Lewis and Smith (31) performed a series of crucible tests on a range of superalloys in the temperature range 700 - 1000°C. Again, pure sodium sulphate was not very aggressive, but the addition of NaCl increased the rate: the mixture giving maximum corrosion varied from 1% NaCl with Incoloy DS to a little over 25% NaCl with Nimonic 80A.

Archdale (2) also reported that sodium sulphate alone failed to corrode Nimonic 90 in a crucible test, but that mixtures of sodium sulphate and sodium chloride gave tumour-like corrosion products which were visually and metallographically similar to those found after the engine run. Similarly, it was observed that mixtures of sodium sulphate and carbon would also give this form of attack. Archdale also found a similar form of attack in a crucible test using 95% $MgSO_4$, 5% carbon at 900° for 72 hours.

It is possible that, since the early investigators generally used the crucible test with very short exposure times, they were looking for a much too rapid rate of attack. In salt-coated tests, several investigators including Hardt et al (38), Goebel and Pettit (47), Bornstein and DeCrescente (48), and Johnson et al (39) have shown that the rate of attack of a number of alloys is greatly enhanced by a coating of sodium sulphate.

Bornstein et al (49) have examined the effect of other additives to the salt on the corrosion of a number of alloys. The addition of 5.5 wt.% V_2O_5 to the sodium sulphate resulted in an oxidation rate of a Ni-1% V alloy at 900°C which was virtually the same as the uncoated alloy. The accelerating effect of the sulphate coating was also greatly reduced by the addition of 5.5 wt.% M_oO_3. A coating of 1 mg/cm^2 of sodium sulphate produced a considerable enhancement in the oxidation of B 1900, but the enhancement was virtually eliminated by the addition of 1 mg/cm^2 Cr_2O_3 to the coating. Conversely, the addition of 1 mg/cm^2 of M_oO_3 increased the attack still further.

Goebel and Pettit (40) reported that 1 mg/cm^2 Na_2SO_4 had little effect on the oxidation of Co-25 Al-12 W at 1000°C, certainly for the first 1000 minutes, but if the system was annealed in argon first, the oxidation was enormously enhanced.

The rate of oxidation of the alloy was also greatly enhanced if the specimen was coated with 1 mg/cm^2 Na_2WO_4, in the absence of any sulphur: a similar result was obtained with a Co-25 Cr-12 W alloy, although the effect was less spectacular; the corrosion rate of Co-35% Cr was not greatly affected by the tungstate coating.

Johnson et al (39) showed that, while the oxidation of cobalt at 900°C was not increased by a coating of Na_2SO_4, it was considerably enhanced by a coating of Na_2SO_4 + Na_2SO_4, and the enhancement appeared to increase as the tungstate content of the salt mixture increased.

Bornstein and DeCrescente (48) showed that B 1900 also suffered accelerated oxidation when coated with sodium nitrate, although the alloy of course did not then contain any sulphates. Johnson et al (39) found that specimens of Co-7.5 wt.% W coated with Na_2CO_3 oxidised initially at about the same rate as the uncoated specimens, but that after about 40 hours at 900°C the rate accelerated to a value comparable with that of the sulphate coated specimen.

3.4. Effect of Alloy Composition

The laboratory tests agree with practical experience that chromium content is the most important factor. There is considerable disagreement about the effect of other alloy elements, perhaps because of interactive effects. Most alloys of this type depend for their oxidation resistance on the formation of either a Cr_2O_3 scale or an Al_2O_3 scale. Generally, for a nickel-base alloy to form a chromia scale it requires 15% Cr or more, and less than 5 wt.% Al; an alloy with over 5 at % Al and more than about 5% Cr will generally form an Al_2O_3 scale. Thus, B 1900 should be an alumina former, and IN 100; 713C will probably also form alumina. Nimonic 105 is a borderline case, and probably could form either Al_2O_3 or Cr_2O_3 externally

depending on the condition. Udimet 500, Udimet 700 and IN 738, on the other hand, should be chromia formers. It might be anticipated that alloys forming these two oxides would behave differently, and that for example the role of molybdenum might be different in each class.

Lewis and Smith (31) appear to have been the first to attempt a systematic study of the effect of alloying elements on the performance of a group of superalloys in a crucible test. They expressed their results in terms of a chromium equivalent,

$$\chi_{LS} = \%\ Cr + 0.7\ (\%\ Al + 1.5\%\ Ti)$$

so that both aluminium and titanium were regarded as beneficial. The alloys they examined included alumina and chromia formers.

Rentz, quoted by Donachie et al (13), used a more complicated expression:

$$\chi_R = \%\ Cr + 3.8\ (\%Al-5) + 2.0\ (\%W) - 12.5\ (\%C) - 1.4\ (\%Mo-1)$$

from which it would appear that aluminium is beneficial at the higher levels; tungsten is beneficial, carbon is deleterious, presumably by tying up chromium as carbide, and molybdenum above very low levels is also harmful.

Ryan et al (43) used a regression analysis to correlate the volume loss due to corrosion in their cyclic test with alloy content and temperature:

$$\begin{aligned}\log_{10}(\text{volume loss}) = {} & 5.85 \times 10^{-9}\ T^3 - 1.34 \times 10^{-5}\ T^2 \\ & + 6.33 \times 10^{-2}\ (\%\ W) + 8.64 \times 10^{-2}\ (\%\ Mo) \\ & - 6.78 \times 10^{-2}\ (\%\ Cr) - 8.98 \times 10^{-2}\ (\%\ Al) \\ & + 11.28\end{aligned}$$

from which it appears that both molybdenum and tungsten are harmful, and both chromium and aluminium are beneficial.

Felix (50) studied the corrosion of a range of nickel-base alloys in a combustor rig at 850°C for 300 hours with 15 ppm Na and 5 ppm V in the fuel, concluding that Al was harmful, while Ti and Cr were beneficial. The corrosion rate increased linearly with the function

$$\frac{\%\ Al}{(\%\ Ti)\ (\%\ Cr)^{\frac{1}{2}}}$$

Kaufman (37) concluded, as a result of his burner rig tests described in Section 3.1, that for Ni-15 Cr base alloys, aluminium increased the corrosion resistance greatly, titanium and cobalt increased it slightly, tantalum had no effect, and tungsten decreased it slightly.

Bergman et al (12), discussing the effect of alloy chemistry on the hot corrosion of alloys in the G.E. Small Burner rig, remarked that for nickel-base alloys increasing chromium is beneficial; increasing cobalt may increase the corrosion resistance somewhat; molybdenum additions are increasingly detrimental as the temperature increases; tungsten has no effect at 955°C but is detrimental at 1038°C; tantalum seems to improve the resistance; titanium is not harmful and may even be beneficial; aluminium additions are increasingly detrimental as a function of temperature in simple alloys, but may be beneficial in complex alloys; rhenium and yttrium have no effect.

Walters (41) showed that chromium was beneficial, but commented that a high chromium content alone was not enough to guarantee corrosion resistance, a point that has been made by others. He did not discuss the effect of other alloy elements in any detail, but suggested that tungsten and aluminium may be helpful at high enough chromium contents, and molybdenum harmful.

Viswanathan (51) used a burner rig to examine the corrosion of a number of nickel-base superalloys using a diesel fuel with 6% sulphur added. Specimens were coated with 50% Na_2SO_4, 50% $MgSO_4$ and hung in the combustion apparatus for times ranging from 10 to 200 hours at 816°C. In this test, Udimet 700 was worse than 713C. Viswanathan added from 0.1 to 0.3% lanthanum and yttrium to Udimet 700, producing a considerable improvement in corrosion resistance: lanthanum was rather more effective than yttrium, and 0.2% La appeared to be an optimum. Seybolt (52) produced a considerable improvement in the corrosion resistance of Udimet 500 by the addition of 0.5% cerium; the test used was a G.E. small burner rig at 955°C for 1000 hours. The principal effect appeared to be a reduction in the degree of internal sulphidation.

Hamilton et al (14) removed 20 713C blades showing gross oxidation and 20 showing only slight oxidation from a single rotor, and found there was a better correlation of the attack with the chromium plus aluminium content than with the chromium content alone.

Stetson and Moore (53) used the Solar gas turbine environmental simulator with JP-5 fuel (0.04 - 0.12% S) and 35 ppm synthetic sea salt injected into the combustion gases to study the corrosion of a range of superalloys at 899° and 983°C. They used a chromium equivalent :

$$X_{SM} = (\% \text{ Cr} + \tfrac{1}{2} \% \text{ Al} - \% \text{ Mo})$$

but the correlation was not very good at the higher temperature.

Clark and Hulsizer (54) conducted 24 or 100 hour cyclic tests at 1600°C to determine the effect of water vapour on the oxidation of a range of superalloys: the total duration of the tests was 400 to 1000 hours, and the water vapour contents were 0.1, 5 and 10%. For some alloys the presence of water vapour had a significant deleterious effect, and the authors suggested that this might be related to the refractory metal content: the higher the content, the greater the effect.

Norman and Harston (55) used the salt shower test to study the hot corrosion of a number of commercial high-chromium nickel-base alloys. The salt used was 75% Na_2SO_4, 25% NaCl; tests were run up to 500 hours, and temperatures were in the range 700 - 900°C. The results confirmed the beneficial effect of chromium. With low chromium alloys (12-16%) it appeared that levels of up to 6% aluminium did not significantly decrease the propensity of the alloys to catastrophic hot corrosion attack. One alloy with significant quantities of molybdenum present was inferior to the other high chromium alloys.

Billingham et al (56) studied the effect of varying the Ti/Al ratio in an alloy which was basically Nimonic 115. The corrosion resistance was determined in the range 800 - 950°C using a simple laboratory salt-spray test. The results showed some improvement in corrosion resistance as the Ti/Al ratio increased.

Morrow et al (57) studied a range of carefully homogenized nickel-base alloys, attempting to determine the relative roles of aluminium and molybdenum. The chromium content was in the range 12.56 - 14.29%, the aluminium content in the range 1.02 - 5.95%, and the molybdenum content in the range 2.0 - 8.61%. Four alloys also contained a little over 3% titanium. The specimens were tested in the G.E. small burner at Lynn using a 1% S diesel fuel, 5 ppm salt, 870°C and 980°C test temperatures, test durations up to 1000 hours, cycling to room temperature every 50 hours. The results showed that for the 4½ and 6% Al alloys at 870°C, the corrosion decreased progressively as the molybdenum content increased from 0 to 9%. There was a maximum corrosion at 2% Mo for both the 3% Al and 1% Al - 3½% Ti alloys, but thereafter the rates again diminished with increasing molybdenum content.

For a given molybdenum content, the attack increased with increasing aluminium content.

The very marked difference between these results and those of the earlier investigations reported above are thought by the authors to be due in part to the very severe conditions used in the early studies, and it is certainly true that the more severe the conditions, the worse all the refractory metals behave in hot corrosion; and in part to the use by the early investigators of as-cast specimens, which would contain significant inhomogeneities. Local enrichment (for example, molybdenum-rich carbides) are known to have a bad effect. The use of a rather borderline chromium content may well have some bearing on the results as well.

As mentioned in Section 3.3., Bornstein et al (49) have shown that in certain cases the addition of MoO_3 to an Na_2SO_4 coating can decrease the corrosion- and they also showed that a Ni-5% Mo alloy coated with sodium sulphate oxidised more slowly than pure nickel similarly coated.

Goebel et al used the salt-coating test to study the hot corrosion of a number of alloys, noting Bornstein and DeCrescente's suggestion (58) that nickel-base alloys containing aluminium might be more susceptible to hot corrosion because the formation of sodium aluminate promotes the formation of oxide ions. The alloys studied included B 1900, and the same alloy without aluminium, without titanium, without molybdenum, without either molybdenum or tantalum, and without molybdenum, tantalum or titanium. At 1000°C, the alloys without aluminium and without titanium oxidised more rapidly than the base composition : all the others oxidised much less rapidly; a simple Ni-8 Cr-6 Al alloy was the slowest of all. Goebel et al distinguish two types of reaction: Na_2SO_4-induced accelerated oxidation, and Na_2SO_4-induced catastrophic oxidation. There is little doubt that the catastrophic corrosion of B 1900 can be attributed to the refractory metals. The metallographic examination of the alloys containing no molybdenum, which underwent accelerated attack, showed a morphology like that observed in practice: beneath a layer of oxide, a layer of mixed metal and oxide, and then a layer containing chromium sulphides in the metal, although the structure was rather coarser than that observed in practice. In the catastrophic oxidation a thick layer of porous oxide developed, with a fairly uniform metal interface: no mixed oxide/metal layer was formed, and there was little or no sulphur penetration. Tungsten or vanadium additions were also able to induce catastophic oxidation of Ni-Al alloys.

Under some circumstances, molybdenum additions can result in catastrophic oxidation in the absence of any external contamination; Leslie and Fontana(59), for example, studied the oxidation of Fe-25 Ni-16 Cr-6 Mo steels in air at 900°C. In flowing air the oxidation resistance was good, but in static air attack was catastropic, suggesting that accumulation of gaseous MoO_3 over the metal may be important. Several other authors have reported similar effects.

Many investigators regard the possible formation of liquid oxides as important, and several compound oxides have relatively low melting points: $MoO_3 . Fe_2O_3$ - 900°C; $MoO_3 . Cr_2O_3$ - 1000°C and $MoO_3 . NiO$ - 1330°C; but lower melting points are possible: there is a eutectic in the system MoO_3-Fe-Fe_2O_3 at 713°C, and this is further lowered to 705°C by an MoO_2 addition.

Johnson et al (60) used a salt-coated test to study the corrosion of Co-Cr-Mo alloys. Co-Cr-4% Mo underwent accelerated oxidation at 900°C if the chromium content was below 20%, but a Co-25 Cr-4 Mo alloy was relatively unaffected. However, a Co-25 Cr-10 Mo alloy underwent catastrophic corrosion, the scale consisting of an outer porous layer of CoO, Cr_2O_3 and MoO_3 and a molybdenum-rich layer apparently containing both MoO_3 and $Na_2 MoO_4$ at the alloy/scale interface. Only small amounts of fine sulphides were present in the alloy.

Peters et al (61) have examined the hot corrosion of a range of nickel-base alloys, the majority based on Ni-15 Cr, using the salt coating method at 900°C. Ternary alloys containing 1, 3, 4, 6 and 10% Mo and quaternary alloys containing Al and Mo were studied for times up to 100h. In simple oxidation tests in flowing oxygen all the molybdenum-containing alloys oxidised at essentially the same rate as the Ni-15 Cr binary; but in static oxygen the molybdenum-containing alloys exhibited breakaway oxidation, the rate accelerating after a few hours. The sodium-sulphate coated specimens containing 0, 1 and 3% Mo corroded at about the same rate: the coating had little effect. The alloys containing 4% Mo and more underwent a breakaway, the rate accelerating very considerably after a few hours. However, although the reaction was undoubtedly catastrophic, there was extensive internal sulphidation and fragmentation of the metal surface, the morphology (shown in Figure 4) resembling quite closely that of the corroded Nimonic 105 blade shown in Figure 2. The corrosion rate for the Na_2SO_4 coated sample was however almost the same for the same alloy in static oxygen, so that (apart from the obvious sulphidation) the role of the salt coat might have been merely to prevent the escape of MoO_3. The quaternary alloys containing aluminium corroded in a similar manner to the ternary Ni-Cr-Mo alloys: if anything, the presence of up to 8% Al increased the rate still further. However, the morphology of the attack was significantly different: for a Ni-15 Cr-8 Al-6 Mo alloy the metal interface was relatively smooth and the internal sulphidation relatively restricted (Figure 5).

It has been suggested that the role of molybdenum might be to react with the sodium sulphate, forming sodium molybdate and making the salt SO_3-rich (acidic). However, Peters showed that a Ni-15 Cr alloy could be severely corroded by a mixture of Na_2SO_4 and Na_2MoO_4, in which the acidity of the salt should presumably be unaffected. This point will be discussed later.

Nagarajan and Stringer (62) have studied the effect of up to 10% Mo on the hot corrosion of Co-25% Cr base alloys in a Dean apparatus at 900°C in air. Increasing molybdenum increased the corrosion rate, and there was clear evidence of a break-away process: with pure Na_2SO_4 there was little attack of any of the alloys for the first 120 hours, but the alloys containing 5% Mo and above were heavily corroded after 170 hours. The addition of Na_2CO_3 to the salt, which should have made the condensate on the specimen Na_2O-rich, greatly enhanced the attack. Later, this work was extended to lower chromium -content alloys, and in this case the addition of Na_2O did not appear to accelerate the attack.

In summary, it is clear that it is impossible to make simple statements of the form "molybdenum is bad for hot corrosion" because it depends what aspect of hot corrosion one is discussing - the initiation of the attack, or its propagation, mildly corrosive or severely corrosive conditions; chromia-forming or alumina-forming alloys; and so forth. The same is true for the effect of aluminium. The effects of most other elements seem by comparison to be insignificant, although particular circumstances may arise where other factors may become critical.

4. Thermochemistry of Hot Corrosion

Simons et al (44) were the first to attempt to describe the chemistry of the process. They suggested that there were two distinct stages: a "triggering" stage associated with the initial reduction of sodium sulphate, involving an unspecified reducing agent R:

$$Na_2SO_4 + 3R = Na_2O + 3RO + S,$$

$$M + S = MS$$

where M is the metal forming the single sulphide MS, for simplicity; and a rapid "autocatalytic destruction' stage:

$$Na_2SO_4 + 3MS = 4S + 3MO + Na_2O,$$

$$4M + 4S = 4MS$$

DeCrescente and Bornstein (24) were the first to consider the thermochemistry of sodium sulphate formation and pointed out that since sodium sulphate was a very stable species the sulphur activity in the vapour phase would be too small to have any effect and that consequently it was necessary for the salt to condense on the metal.

Quets and Dresher (63) were the first to suggest the use of predominant phase diagrams, often referred to as Pourbaix-Ellingham

diagrams, to describe the possible course of the reaction, and this has been a most useful development. A similar analysis was presented by Gulbransen and Jansson (64). The relevant diagrams have recently been collected by Stringer (3). These diagrams can be presented either with the two axes representing the sulphur and oxygen activities respectively; or with the vertical axis representing the oxygen partial pressure and the horizontal axis the SO_3 partial pressure. The latter method has the advantage that the horizontal axis is then also the oxygen ion activity in the molten sodium sulphate; but the disadvantage is that it implies a particular model for the corrosion process, and it is difficult to translate the information to (for example) the not-dissimilar corrosion of alloys in gas mixtures. The two representations are of course exactly equivalent: it is possible to draw lines of constant sulphur activity on the latter, or lines of constant SO_3 activity on the former.

Figure 6 shows the Ni-O-S system at 1200K plotted according to the first convention (63), and Figure 7 shows the phases in the Al-O-S system that are in equilibrium with Na_2SO_4 at 1000°C (65). All these diagrams are calculated making a number of assumptions, most important that the phases are distinct and at unit activity. Actually, this is far from the truth: thus, Figure 8 shows the Na-O-S diagram at 1000°C, but in fact in the liquid there is a continuous solution between Na_2O, Na_2S and Na_2SO_4, so that these boundaries are very approximate.

Hardt et al (38) suggested that the overall corrosion reaction could be written

$$Na_2SO_4 + {}^9/_2\,Ni = Na_2O + 3NiO + \tfrac{1}{2}\,Ni_3S_2$$

and Quets and Dresher (63) claimed that consideration of the diagrams shown in Figures 6 and 8 proved that this equation was incorrect, because there was no possible oxygen and sulphur activity at which the phases Na_2O, NiO and Ni_3S_2 could coexist. However, this criticism is only valid if the phases are considered to be at unit activity: in practice, of course, the Na_2O would be in solution in the liquid Na_2SO_4 and thus at an activity appreciably less than unity.

Furthermore, in considering the overall corrosion situations it should be recognised that the sulphur and oxygen activities vary continuously through the whole system: high oxygen, low sulphur in the gas; a gradient perhaps within the salt layer producing high sulphur, low oxygen at the salt/oxide interface; to low sulphur, low oxygen deep within the metal. Stringer and Whittle (66) have suggested that a "reaction path" could be constructed on the stability diagrams, thus showing the sequence of phases in the different layers of the reaction systems.

5. Hot Corrosion Mechanisms

5.1. The Role of Sulphur

In much of the early literature, great importance was attached to the sulphides present ahead of the oxidation front; indeed the reaction was often referred to as "sulphidation", although this is a misleading term whose use should be discouraged. Danek (67) reviewed the early literature, quoting three schools of thought for the mechanism of the corrosion:

(a) Sulphur reacts with the chromium to form lavender-grey globules of Cr_2S_3. As a result, the matrix oxidises rapidly and flakes off, carrying sulphide globules with it.

(b) Cr_2S_3 is formed, but when oxygen is available as a result of the advance of the metal/oxide interface, the sulphide oxidises together with the matrix releasing sulphur for further attack.

(c) The globules that are observed to be Cr_2S_3 at room temperature have in fact been Ni_3S_2 at temperature, forming a liquid phase which oxidises readily.

Seybolt and Beltran (68) conducted experiments on the reaction between nickel and sodium sulphate in vacuum, finding considerable sulphur penetration; the remaining salt gave a highly alkaline aqueous solution, suggesting an excess of Na_2O. On the basis of these and other results, they concluded that in hot corrosion the metal reacted with the sulphate to form a liquid sulphide phase which was preferentially oxidised, releasing sulphur for further reaction. However, a Ni-20 Cr alloy did not form nickel sulphide until virtually all the chromium had reacted to form chromium sulphide.

Tedmon and Seybolt (69) tested the hypothesis that chromium sulphides might oxidise more rapidly than the matrix, but found that a Cr_7S_8 specimen oxidised at about the same rate as pure chromium at 1050°C, forming a protective Cr_2O_3 coat, and a similar result was reported by Goebel and Pettit (47), who sulphidized a Ni-Cr alloy to form a continuous external layer of "CrS" and then oxidized it: the oxidation rate was again the same as for the unsulphidised material.

Bornstein and DeCrescente (48) studied the oxidation at 900°C of three superalloys (B 1900, Udimet 700 and Waspaloy) after impregnating them with as much sulphur as is present in a $1 mg/cm^2$ coating of Na_2SO_4. The impregnation was carried out by heating the specimen with sulphur in an evacuated quartz capsule for 16 hours at 900°C, forming a layer some 10 μm thick with fine sulphide particles dispersed in it. The presulphidation had virtually no effect on the

subsequent oxidation, and the authors concluded that the formation of sulphides in hot corrosion was incidental, and did not play an important part in the reaction.

Spengler and Viswanathan (69), on the other hand, presulphidized Ni-15 Cr specimens in 0.2% SO_2-N_2 mixture at 871°C for 1, 6, 30 and 50 hours, and then oxidised them at the same temperature. The oxidation of the presulphidized specimens was much faster than that of the unsulphidized, and a morphology quite similar to that observed in hot corrosion developed. Erdös (5) remarked that while it was possible to reproduce the corrosion morphology quite well by oxidizing presulphidized 713C, the oxide formed was different.

El-Dahshan et al (70) studied the oxidation after presulphidation of a number of Co-Cr and Co-Cr-C alloys in the temperature range 800-1000°C using sulphur pressures above and below the dissociation pressure of cobalt sulphide. When a thick continuous sulphide layer was formed, the oxidation rate was essentially unaffected, resembling that of the pure metal. However, if the initial sulphide layer was thin, it speedily became discontinuous, and then a hot corrosion-like morphology developed during subsequent oxidation. Even in cases where only chromium sulphide had been formed initially, it was possible for the subsequent oxidation to push the sulphur activity beneath the oxide surface high enough that cobalt sulphide formed. The role of sulphur in hot corrosion has been discussed at length by Stringer and El-Dahshan (71) who conclude that the development of the characteristic hot corrosion morphology can be wholly explained in terms of sulphidation models. In the case of chromia formers, the sulphides formed in most cases are chromium rich, and are not liquid at temperature; they are preferentially oxidised, leaving the chromium depleted metal islands embedded in chromium oxide. It is possible that small amounts of nickel sulphide are formed at the oxide/chromium sulphide interface, as suggested by McKee et al (19), since chromium sulphide dissolves an appreciable amount of nickel but chromium oxide does not; however, if it is present, it does not appear to play an important part in the corrosion. The sulphur liberated by the oxidation does not in general escape through the oxide, but moves inwards, sulphidizing more chromium. As a result, the reaction is self-maintaining. In some cases, it is possible for the sulphur activity to rise high enough for large amounts of nickel sulphide to be formed. This is then liquid: there is rapid degradation of the alloy, but the sulphide morphology is quite different to that customarily seen in hot corroded specimens. Nickel sulphides are incorporated into the oxide scale. There is no evidence of a rapid exchange reaction converting the nickel sulphide to chromium-sulphide during cooling.

In the case of alumina formers, a different mechanism is possible. Again, chromium sulphides are formed but this depletes the surface layers in chromium, which appears to destroy the ability of the alloy

to form an external Al_2O_3 scale; the aluminium oxidizes internally. In this case, the sulphur resulting from the oxidation of the sulphides does escape through the scale as sulphur oxides; and the reaction is not self-maintaining. The development of the microstructure is not due to the oxidation of the sulphides, as in the former case, but due to the continuing internal oxidation of the reactive elements. Stringer and El-Dahshan show cross-sections of specimens of Nimonic 105 (a) presulphidized and oxidized, and (b) oxidized with a sodium sulphate coating: the morphologies are very similar indeed, and both closely resemble hot corrosion morphologies encountered in practice.

5.2 The Salt-Fluxing Models.

However, although several investigators have been able to reproduce hot corrosion morphologies in the absence of salt, a number of other investigators have been able to reproduce some aspects of the reaction without the presence of sulphur. Thus, Bornstein and DeCrescente in a number of the publications referred to above have shown that specimens coated with $NaNO_3$ or Na_2CO_3 underwent rapid oxidation in a manner very similar to specimens coated with Na_2SO_4, and observations of this kind led them to postulate the salt-fluxing model, and this has been developed further both by these authors and by Goebel and co-workers. The following account is drawn from Goebel et al (47,65).

Consider first the oxidation of pure nickel covered with a coating of molten sodium sulphate. Initially,an adherent layer of NiO forms on the metal surface, raising the sulphur activity in the salt adjacent to the oxide surface; sulphur then penetrates through the oxide from the sodium sulphase forming a layer of nickel sulphide immediately below the oxide. The removal of this sulphur has the effect of displacing the stoichiometry of the sodium sulphate to the Na_2O-rich side (that is, the salt becomes basic) and the oxide ion activity rises. Eventually, it is postulated, it rises high enough to oxidise the nickel oxide according to the reaction

$$NiO + O^{=} = NiO_2^{=}$$

This nickelate ion migrates through the salt, until near the salt/oxygen interface, where the salt is more nearly stoichiometric and the oxygen ion activity is lower, the reaction goes to the left, precipitating nickel oxide. This clearly results in the development of a porous, non-protective oxide layer. However, as Goebel and Pettit point out (47) this reaction is not self-sustaining, since the high oxide ion activity required to form the nickelate ion can only be established in the early part of the reaction, since with a fixed amount of sodium sulphate only a limited amount of sulphur can be removed. So the reaction slows down, and a continuous protective NiO layer is re-established at the metal surface. This model,

which the oxide is dissolved by its being oxidised by a basic salt to form an anionic species, is called the basic fluxing model. Clearly, basic fluxing can be inhibited by the presence of a species which will react with the excess Na_2O to form a stable compound (or, to put it another way, react with the excess oxide ions to form a more stable anion), and a good example is Cr_2O_3. Thus, coating nickel with a mixture of sodium sulphate and Cr_2O_3 does not produce accelerated oxidation, and a Ni-5 Cr alloy coated with Na_2SO_4 does not undergo accelerated attack.

As mentioned before, Goebel et al (65) now distinguish two types of Na_2SO_4 - accelerated corrosion of nickel base alloys: a catastrophic form, where the morphology of the reaction product is such that the oxidising environment has virtually free access to the alloy surface, and an accelerated form where the products of oxidation do inhibit the reaction but not to the extent that they would in the absence of sodium sulphate.

In principle, it might appear that a Cr_2O_3 scale could also be fluxed by the mechanism, and indeed it can: while fluxing NiO requires sulphur removal to increase the oxide ion activity to the point where the nickelate ion is stable, the chromate ion is stable in reagent grade sodium sulphate; as a result, there is no precipitation of a porous oxide, no internal sulphidation; as soon as the oxide ion activity has been lowered sufficiently in the salt a protective oxide layer is established. These mechanisms can be interpreted in terms of the phase stability diagram shown in Figure 7, the cross showing the oxide ion activity in reagent grade Na_2SO_4, and the dashed lines showing the postulated changes resulting eventually in the basic fluxing of Al_2O_3.

The catastrophic oxidation appeared to be related to the presence of molybdenum, although other experiments showed that tungsten and vanadium could produce similar effects. The oxide ion activities in a molten sodium sulphate/potassium sulphate/lithium sulphate eutectic mixture were determined electrochemically, and the effect of adding Na_2O_3, Cr_2O_3, WO_3, MoO_3 and V_2O_5. The first increased it, as would be expected, but all the rest decreased it, producing in other words more acidic salt. Examination of Figure 7 shows that if the oxide ion activity falls far enough, a different fluxing mechanism, in which the metal ion enters the salt as a cation, is possible: this is called acidic fluxing. Note here that it isn't necessary for any sodium sulphate to be present, if the activity of (for example) MoO_3 were high enough to remove oxide ions from Cr_2O_3 or Al_2O_3 to form a $MoO_4^=$ ion, then acidic fluxing of the chromia or alumina will take place. However, the observation that sodium molybdate/sodium sulphate mixtures can produce a similar form of attack is difficult to explain on this model.

Goebel et al consider that the chemistry of the salt is first

modified by the solution of (for example) molybdenum-rich second phase particles above which, perhaps, the protective oxide is not continuous. The locally acidic salt then fluxes the nearby oxide, and the reaction spreads over the metal surface. Because MoO_3 is continually formed in the Na_2SO_4 next to the alloy surface as the alloy corrodes, acidic fluxing is self-sustaining.

There is no doubt that catastrophic destruction of alloys can occur by the acidic fluxing mechanism suggested by Goebel et al, but it is worth asking whether or not the process occurs in actual hot corrosion. The morphology of the reaction is significantly different from that normally encountered, but on the other hand the form of the scale and the general pattern of susceptibility does resemble that in practice. Does basic fluxing occur in practice? The difficulty of sustaining the reaction may seem to be a problem, but it is possible that in practice the salt is continually removed and replaced, and in that case it would be possible to sustain the reaction. Both mechanism requires an oxide ion gradient to be established across the salt layer. This implies that diffusion in the salt layer is relatively slow: a layer of 1 mg/cm^2 of sodium sulphate would be only 4μm thick or so. But in that case the establishment of the necessary gradient should also be relatively slow, taking perhaps a few minutes; and it is not clear that the time of residence of the salt on the surface will be that long. If the surface is covered with a porous oxide, there is good evidence that the salt permeates the oxide, extending close to the metal surface. This would have the effect of stabilising the salt layer, and increasing its effective thickness: as will be seen later, it is possible that other processes effectively shielding the salt from removal can take place rapidly.

The effect of carbon on sodium sulphate is to reduce it: traces of Na_2S can be detected in sodium sulphate/carbon mixtures after cooling from the melt. The sulphur potential is thus greatly increased, and this probably (but not necessarily) implies an acidic shift in the salt. The probable major effect of the carbon would appear to be an increase in sulphidation, rather than a change in fluxing mechanisms.

Sodium chloride would also appear to have little effect on the basicity of the salt. It has been suggested that it lowers the viscosity of the salt, making it easier to permeate the porous oxide, and in discussion to the paper by Simons et al (44), Dravnieks suggested that the sodium chloride could help in triggering the reaction electrolytically due to surface inhomogeneities setting up local cells. However, it seems likely that the fluxing model cannot easily explain the role of sodium chloride.

5.3. Hot Corrosion as a Two-Stage Process

Several authors have suggested that hot corrosion is a two-stage process, with an incubation period during which nothing much happens, followed by an initiation of the reaction, after which the corrosion propagates rapidly. There is some reason to believe that the practical reaction has this form, although as explained above it has not definitely been established. The first suggestion of a two-stage process was that of Simons et al (44) described in Section 4: they termed the incubation period the triggering stage, and the propagation stage that of autocatalytic destruction.

Stringer and Whittle (72) remark that the initiation of the reaction is associated with the destruction of an initial protective oxide layer, and that several different mechanisms appear to be possible. These include the fluxing of the scale by one of the mechanisms described above, or the mechanical fracturing of the scale by thermal cycling or the mechanical straining of the substrate. Stringer et al (73) have shown a dramatic example of the initiation of hot corrosion on 713C by thermal cycling in a Dean rig test, and Hancock (74) has also been able to initiate hot corrosion both by thermal cycling and mechanical straining.

On several alloys the failure of the scale appears to be quite local, and the salt then penetrates beneath the scale, extending rapidly along the interface until the whole scale layer has separated. Goebel and Pettit have made a film showing this sort of behaviour using a hot-stage microscope. Clearly, the salt has then only limited access to the air, and it would be expected that the sulphur potential would rise rapidly, leading to sulphidation of the essentially bare metal surface.

The acidic fluxing of scale resulting from the solution of refractory metal-rich phases is another mechanism capable of producing local breakdown.

Hurst et al (75) have been able to show that the presence of sodium chloride vapour can induce mechanical failure of the scale, and the authors suggest that this is caused by the chloride reaching the metal surface and reacting there to form a volatile oxychloride.

The second stage is the propagation of the attack, and it is during this stage that the characteristic hot-corrosion morphology develops. The propagation may occur either by the sulphidation/oxidation mechanism described in Section 5.1, or one of the salt-fluxing processes described in Section 5.2. Notice that the salt fluxing may not involve the oxide at all, but direct fluxing of the metal as a cation (acidic fluxing). Since the important criterion for the propagation stage must be the morphological development, the evidence is rather stronger for the sulphidation model; but the salt-

fluxing model probably gives a better explanation of the effect of alloy elements. Part of the problem is that many laboratory tests are really unrepresentative of the detailed reaction, and it must be remembered that one is looking for mechanisms for hot corrosion in the gas turbine and not for the mechanism of corrosion in some particular laboratory test.

5.4. Electrochemical Models of Hot Corrosion

The idea that hot corrosion involves an electrochemical mechanism is as old as the subject. Simons et al (44) in their early experiments used electrolysis as a means of triggering the reaction: the cathode was much more heavily attacked than the anode. As has been remarked, in discussion Dravnieks suggested that in the practical situation the triggering involved the establishment of local cells on the surface. Several workers have used electrochemical measurements for assessing hot corrosion resistance: the work of Shores has been referred to above (35) and Cutler and Grant (76) have made similar studies. Cutler and Grant note the presence of chloride ions can have a significant effect on the activity of transition metal ions in molten alkali sulphate solutions. Rahmel (77) has examined some aspects of corrosion in fused salts from this point of view and May et al (78) have used linear polarization method to study corrosion in a variety of melts containing vanadium. Recently, Vasantasree and Hocking (79) have discussed the electrochemical interpretation of hot corrosion, and have pointed out that because of the high temperatures at which they come molten, the molten salt could provide rapid diffusion paths for the reactant species without the salts themselves taking part in anionic or oxyanionic reactions, and that molten salts are thus capable of both chemical and ion associated reactions.

It is obvious that the acidic and basic fluxing reactions described in Section 5.2 could equally well be expressed in electrochemical terms, and the displacements on the thermodynamic equilibrium diagrams referred to potentials, as in Pourbaix diagrams. For this approach to be useful, it would be necessary to identify local cells on the corroding surface, and of course cracks or holes in the scale through which molten salt could come in contact with the metal might act in this way. However, it must be reiterated that the major damage in hot corrosion is associated with the morphological development of the two-phase oxide/metal layer, and it would be necessary for an electrochemical model to address this problem as well.

Several laboratories are now examining electrochemical approaches to, and models of, hot corrosion; and this work may be most helpful in evaluating some of the part processes in the reaction.

6. Summary

Hot corrosion is a process of accelerated oxidation of particular concern in gas turbines, and is related to the presence of certain impurities in the fuel or on the metal surface, but it is not clear whether this layer arrives as a result of condensation or impaction. The most important constituent of the molten salt layer appears to be sodium sulphate, but sodium chloride, heavy metal cations, and carbon may also be important. The characteristic of hot corrosion is the morphology of the reaction products, in which there is a relatively thin outer oxide layer, a thick mixed oxide/metal layer, and a thin layer in the metal immediately ahead of the mixed layer containing sulphides. In the large majority of cases these sulphides are chromium-rich, but in some cases in exceptionally severe conditions liquid nickel-rich sulphide may develop, leading to very rapid degeneration of the metal. Hot corrosion occurs only above a threshold temperature of the order of 750°C and below a terminal temperature of the order of 950°C, although both these temperatures depend on the alloy composition and the detailed corrosive conditions.

Corrosion resistance is related to chromium content: in nickel-base alloys at least 15% Cr is required for good hot corrosion resistance, although high chromium content does not of itself guarantee good corrosion resistance. There is no general agreement on the effect of other alloy elements, although the majority view is that molybdenum is harmful.

Hot corrosion probably requires initiation, and this may be related to the break-down of the protective scale, which can be mechanical or chemical. After this the reaction propagates, and a model in which the alloy is sulphidised and the chromium-rich sulphide oxidised seems capable of explaining the morphological developments. Salt fluxing mechanisms may also be involved, but not all the experimental observations have yet been satisfactorily interpreted. Electrochemical models of the corrosion have been offered, but are as yet in an early stage of development.

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TABLE 1 APPROXIMATE COMPOSITIONS OF ALLOYS MENTIONED IN THE TEXT

Alloy	Ni	Co	Cr	Al	Ti	Mo	W	Ta	Other
B1900	bal	10	8	6	1	6	-	4.3	
Hastelloy X	bal	1.5	22	-	-	9	-	-	18 Fe
IN 100	bal	15	10	5.5	4.7	3	-	-	1 V
713C	bal	-	12.5	6.1	0.8	4.2	-	-	2 Nb
IN 738	bal	8.5	16	3.4	3.4	1.8	2.6	1.8	1 Nb
Mar-M 421	bal	9.5	15.8	4.2	1.8	2	3.8	-	2 Nb
Mar-M 432	bal	20	15.5	2.8	4.3	-	3	2	2 Nb
Mar-M 509	10	bal	24	-	0.2	-	7	3.5	0.6C
Nimonic 80A	bal	-	20	1	2.2	-	-	-	
Nimonic 90	bal	18	20	1.4	2.4	-	-	-	
Nimonic 100	bal	20	11	5	1.5	5	-	-	
Nimonic 105	bal	20	15	4.5	1.2	5	-	-	
Nimonic 115	bal	15	15	5	4	3.5	-	-	
Udimet 500	bal	18	19	2.9	2.9	4	-	-	
Udimet 700	bal	18.5	15	4.2	3.5	5.2	-	-	
Udimet 710	bal	15	18	2.5	5	3	1.5	-	
Waspaloy	bal	13.5	19.5	1.4	3	4.3	-	-	
X-40	10	bal	25.5	-	-	-	7.5		0.5C

TABLE 2 RESULTS OF ASTM ROUND ROBIN TEST (36)

Ranking of Alloy by Participant

Alloy	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
U 500	1	2	2	2	1	3	1	1	3	3	3	3	1	3	1
IN 738	2	1	1	3	3	2	3	2	2	2	1	2	3	1	2
Mar-M421	3	3	3	4	4	1	2	4	1	5	2	1	2	2	3
U 700	4	4	4	1	2	4	4	3	4	1	4	4	4	4	4
713 C	5	6	5	5	6	5	5	5	5	6	6	5	5	5	5
IN 100	6	5	6	6	5	6	6	6	6	4	5	6	6	6	6

G is a static rig, specimens coated with 50% Na_2SO_4, 50% NaCl and exposed to simulated combustion atmosphere.

H is a high pressure rig, 15 atm.

K is a crucible test with 90% Na_2SO_4 10% NaCl.

N is a high-velocity rig, Mach 1.

The remainder are a variety of burner rigs. In most cases the test temperature was 899°C and the test duration was 100 hours.

Figure 1(a) The corrosion on the concave surface of a Nimonic 100 first-stage turbine blade from an Olympus engine after 401 hours running.

1(b) An unetched section of a similar blade in a badly affected region.

1(c) The corrosion product morphology: an outer layer of porous oxide, a thick layer of mixed metal and oxide, an inner layer of fine sulphide particles in a metal matrix. (x 250)

1(d) The innermost layer, showing the sulphides. It is clear that the oxide particles have been formed by the oxidation of the sulphides. (x 1050) All these figures are from Smith et al (7).

Figure 2 Heavy internal sulphidation at the trailing edge of an originally pack aluminised Nimonic 105 turbine blade from a Proteus engine. From Condé (6) (Crown Copyright Reserved).

Figure 3 Condensation temperatures for Na_2SO_4 as a function of concentration and pressure. From Bessen and Fryxell(23).

Figure 4 Heavy internal sulphidation of a Ni-15Cr-6 Mo alloy coated with 2.07 mg/gm^2 Na_2SO_4 and oxidised for 22 hours at 900°C. Note the general similarity to Figure 2. From Peters et al (61).

Figure 5 Cross-section of a Ni-15 Cr-6 Mo-8 Al alloy coated with 2.68 mg/cm^2 Na_2SO_4 and oxidised for 7 hours at 900°C. There is a thick porous oxide coat, but a relatively smooth metal surface and very little internal sulphidation. From Peters et al (61).

Figure 6 The phase stability diagram for the system Ni-O-S at 927°C. From Quets and Dresher (63).

Figure 7 A phase stability diagram representing the phases in the Al-O-S system that are stable in Na_2SO_4 at 1000°C. From Goebel et al (65).

Figure 8 The phase stability diagram for the system Na-O-S at 927°C. From Quets and Dresher (63).

Figure 1(a)

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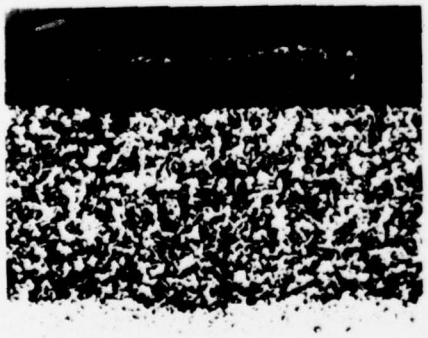
Figure 1(b) An unetched section of a similar blade in a badly affected region.



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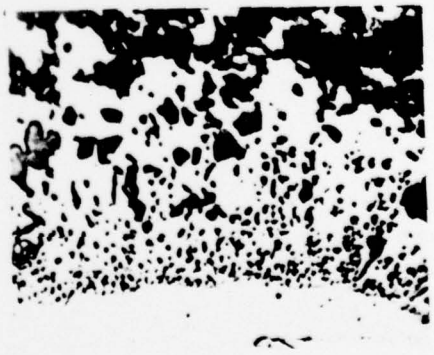

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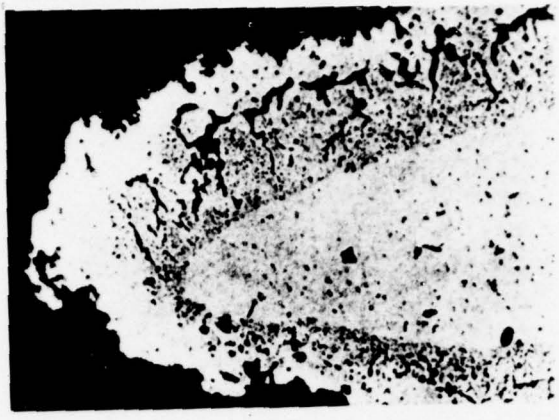

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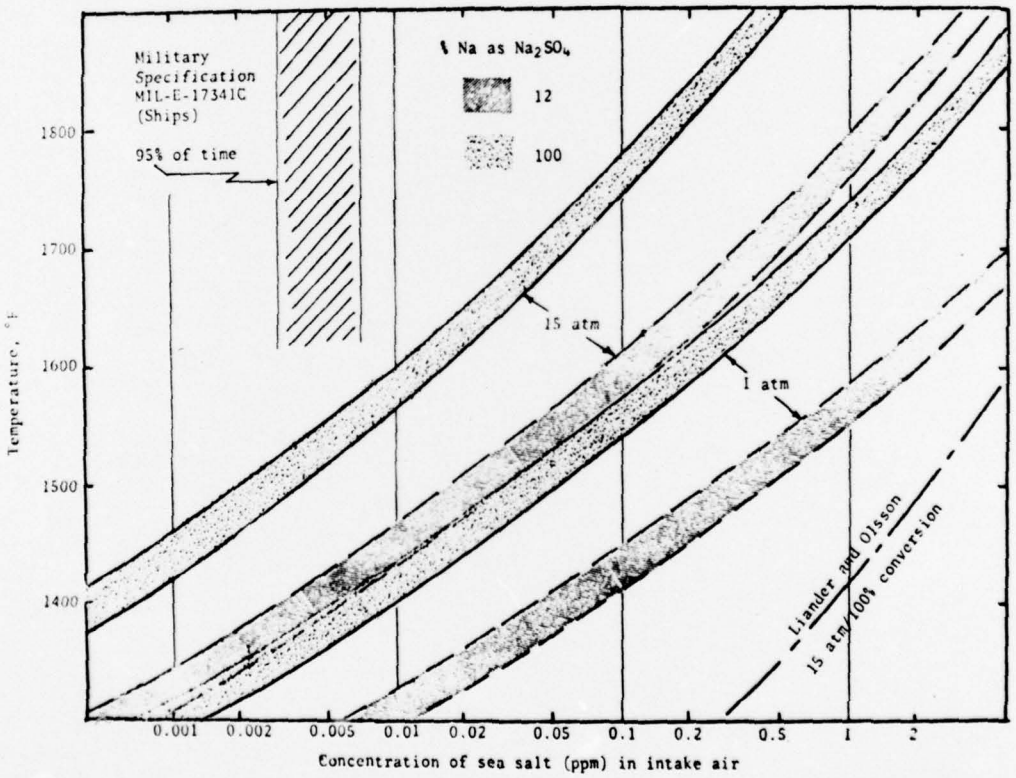

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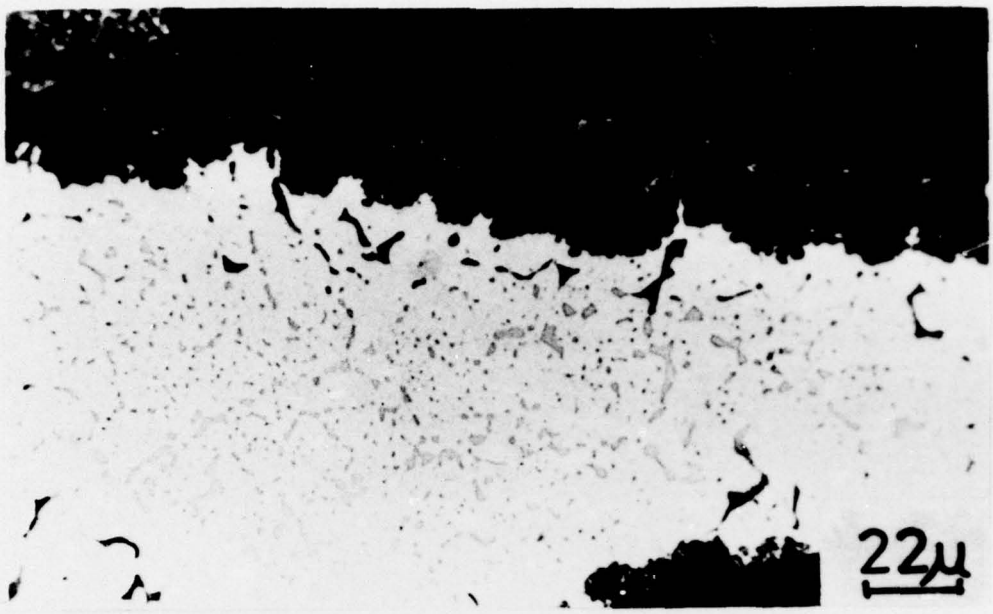

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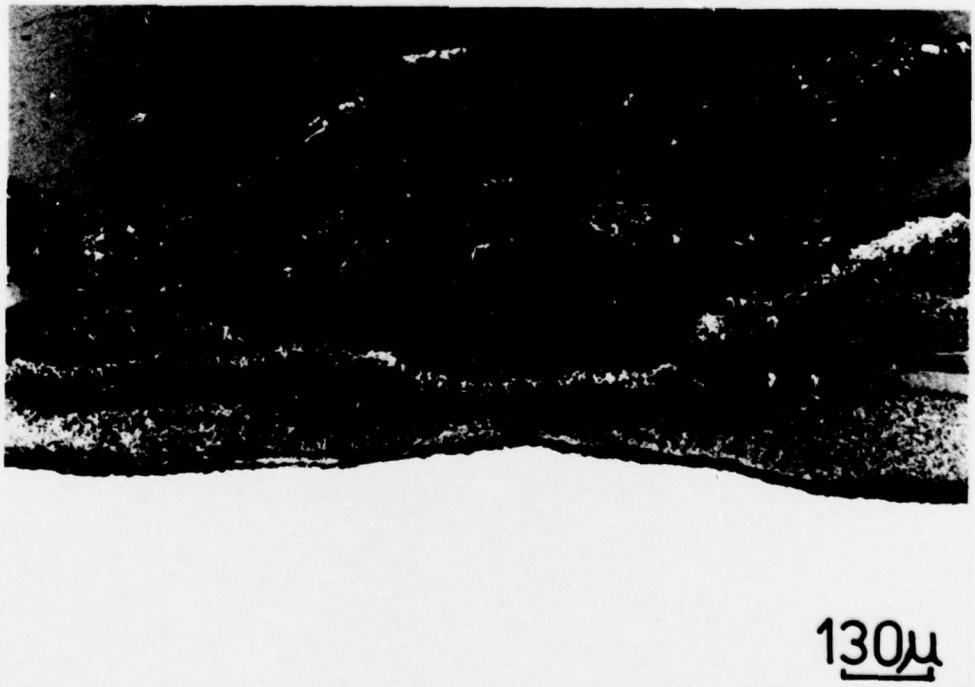

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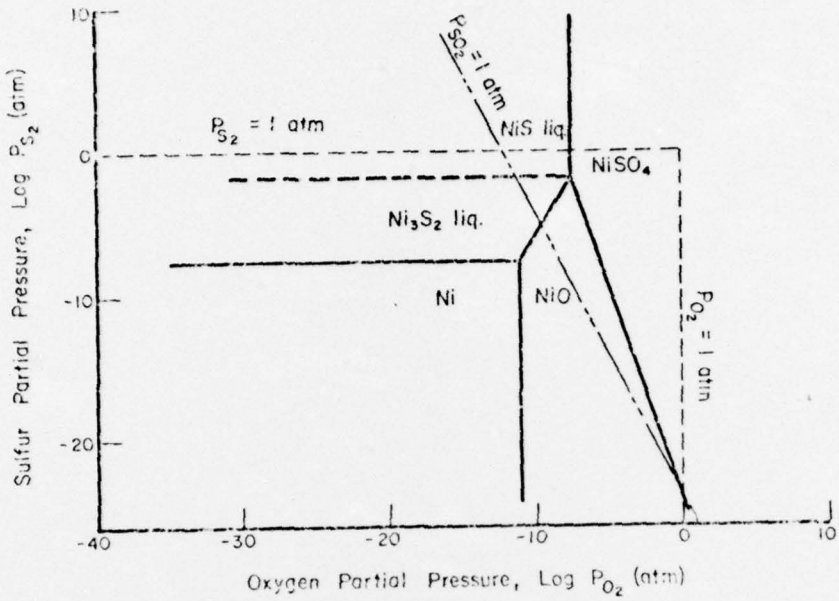

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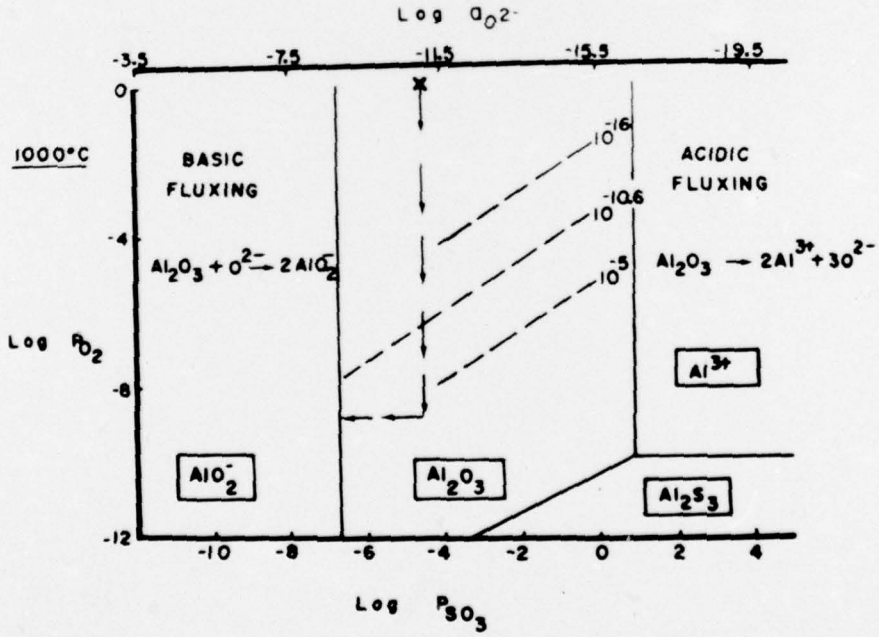

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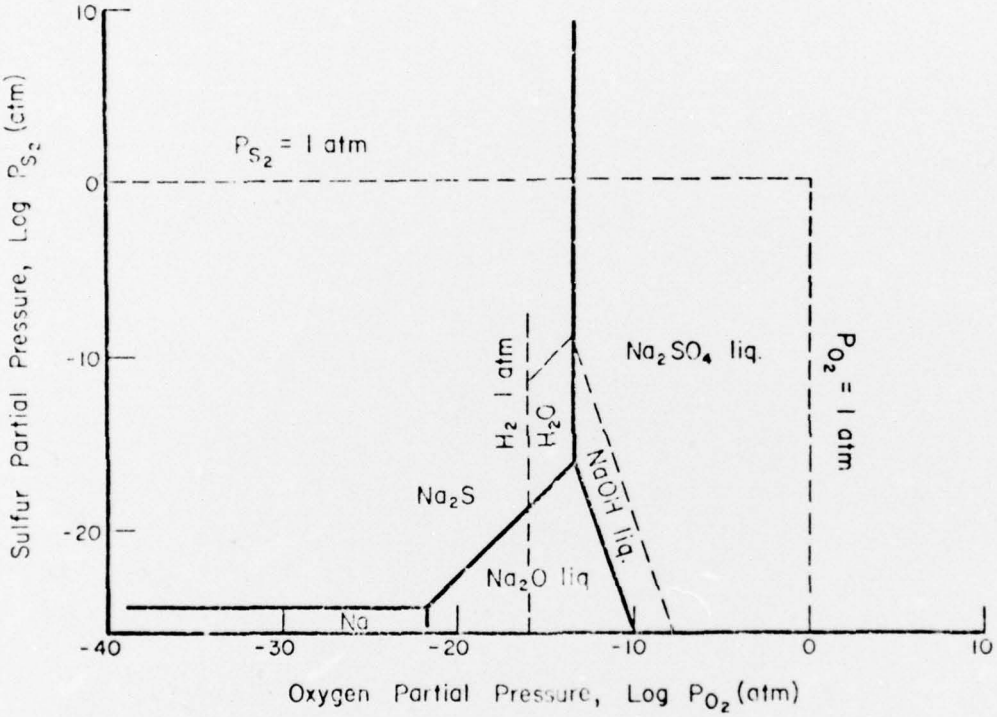

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